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# Alginic acid gels: the effect of alginate chemical composition and molecular weight

**K.I. Draget, G. Skjåk Bræk & O. Smidsrød**

*Norwegian Biopolymer Laboratory, Department of Biotechnology, Norwegian Institute of Technology, University of Trondheim, N-7034 Trondheim, Norway*

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The effect of chemical composition and sequence and molecular weight of different alginate samples on the final properties of alginic acid gels have been studied. It is shown that alginates with a high content of guluronic acid blocks give gels of a considerably higher strength compared to alginates rich in mannuronate. A high fraction of homopolymeric blocks seems to favour the formation of junction zones. Compared to Ca–alginate gels, a more extended molecular weight dependent regime is observed. Kinetic measurements show an initially rapid (~30 min) sol–gel transition with an apparent equilibrium in the dynamic storage moduli gradually obtained within 24–48 h, depending on the chemical composition of the alginate sample used. Mechanical spectroscopy reveals gels with a high degree of solid-like nature, with an increasing frequency dependence with decreasing molecular weight.

## INTRODUCTION

Alginic acid is the protonized, water-insoluble form of its more well known salt equivalent alginate. Alginates and alginic acid must be regarded as a family of unbranched binary copolymers of (1 → 4) linked β-D-mannuronic acid and α-L-guluronic acid (Painter, 1983). The $pK_a$ values of the two monomers have been found to be 3·38 and 3·65, respectively, in 0·1M NaCl (Haug, 1964). The $pK_a$ of the alginate polymer will differ slightly from those of the monomeric acid residues and depends both on ionic strength of the solvent and the alginate concentration (Haug, 1964). It is a well known and well studied fact that an abrupt pH decrease in an alginate solution causes a precipitation of alginic acid molecules (Haug & Larsen, 1963; Myklestad & Haug, 1966; Haug *et al.*, 1967).

It is also well known that an alginate solution, under proper conditions, may form gels by a lowering of pH below the $pK_a$-value of the uronic acid residues (King, 1983). These gels, often just called 'acid gels', have been proposed to be stabilized by intermolecular hydrogen bonds (Atkins *et al.*, 1971). There is, however, very little detailed molecular understanding and surprisingly few reports in the literature which describe the effect of polymer variables on the properties of these gels. The authors of this paper are, in fact, not aware of any papers which have systematically undertaken a study of this kind.

The scope of this paper is therefore to establish a system which reproducibly can form alginic acid gels. These gels have, in turn, been examined to clarify the effects of polymer variables such as chemical composition, monomer sequence and molecular weight on gel strength. Additionally, dynamic rheological tests were performed to reveal the kinetics of the sol–gel transition as well as final gel properties.

## MATERIALS AND METHODS

Table 1 shows the chemical composition and sequence, intrinsic viscosity in 0·1M NaCl and the viscosity average molecular weight of the alginate samples used in this study. The viscosity average molecular weight was calculated from the Mark–Houwink equation and adapting $a$ and $K$ values from Martinsen *et al.* (1991) for the *Laminaria hyperborea* stipe alginates, and from Smidsrød (1970) for the *Laminaria hyperborea* leaf alginates. Chemical composition and sequential parameters were determined by $^1$H-NMR analysis as described by Grasdalen (1983). Alginate samples 1–12 were kindly provided by Pronova Biopolymer A/S, Drammen, Norway.

**Table 1. Chemical composition, intrinsic viscosity and viscosity average molecular weight of the alginate samples used in this study**

| Sample | $[\eta]$ dl/g | $Mw$ (kDa) | $F_G$ | $F_{MG,GM}$ | $N_{G>1}$ | $N_{M>1}$ |
|---|---|---|---|---|---|---|
| #1 *L. hyperborea* stipe | 14·8 | 400 | 0·66 | 0·12 | 14 | 3·2 |
| #2 *L. hyperborea* stipe | 11·6 | 320 | 0·68 | 0·11 | 14 | 3·2 |
| #3 *L. hyperborea* stipe | 10·1 | 280 | 0·66 | 0·09 | 14 | 3·2 |
| #4 *L. hyperborea* stipe | 7·2 | 210 | 0·69 | 0·12 | 14 | 3·2 |
| #5 *L. hyperborea* stipe | 5·2 | 160 | 0·68 | 0·16 | 14 | 3·2 |
| #6 *L. hyperborea* stipe | 3·0 | 100 | 0·70 | 0·10 | 14 | 3·2 |
| #7 *L. hyperborea* stipe | 1·7 | 60 | 0·70 | 0·11 | 14 | 3·2 |
| #8 *L. hyperborea* leaf | 14·2 | 710 | 0·50 | 0·19 | 8 | 4·5 |
| #9 *L. hyperborea* leaf | 13·1 | 655 | 0·48 | 0·18 | 8 | 4·5 |
| #10 *L. hyperborea* leaf | 11·0 | 550 | 0·50 | 0·19 | 8 | 4·5 |
| #11 *L. hyperborea* leaf | 7·6 | 380 | 0·52 | 0·19 | 8 | 4·5 |
| #12 *L. hyperborea* leaf | 5·0 | 250 | 0·53 | 0·23 | 8 | 4·5 |
| #13 *Durvillea antarctica* | 8·0 | n.d. | 0·34 | 0·21 | 5·3 | 5·5 |
| #14 *Ascophyllum nodosum* (Fruiting bodies) | 7·7 | n.d. | 0·26 | 0·05 | 4·0 | 8 |
| #15 *Pseudomonas aeruginosa* | 10·5 | n.d. | 0·40 | 0·40 | 0 | 3* |
| #16 *Pseudomonas aeruginosa* | 11·6 | n.d. | 0·07 | 0·07 | 0 | 13* |

$[\eta]$ = intrinsic viscosity, $Mw$ = viscosity average molecular weight, $F_G$ = fraction of guluronic acid residues, $F_{GM/MG}$ = fraction of alternating sequences.
$N_{G>1}$ = typical average length of guluronic acid blocks larger than 1.
$N_{M>1}$ = typical average length of mannuronic acid blocks larger than 1.
*$N_M$ values based on random distribution of guluronic acid residues.
n.d. = not determined.

### Gelling system

Direct addition of the slowly hydrolysing D-glucono-$\delta$-lactone (GDL) into a solution of sodium alginate was chosen as a method to make alginic acid gels. A systematic study was carried out on the amount of GDL required to obtain an apparent maximum in gel strength. The gels were formed by pouring the alginate/GDL-solution into tissue culture plates with 24 wells with dimensions of 16 mm (diameter) × 18 mm (height) (Costar, Cambridge, MA, USA).

### Gel strength measurements

After 2 days, the gel cylinders were taken out of the wells and a longitudinal deformation test was performed in a Stevens LFRA Texture Analyzer (St Albans, Herts, UK) at a deformation rate of 0·2 mm $s^{-1}$ and a force/deformation curve was obtained. Apparent Youngs modulus ($E_{app}$) was estimated from the initial slope ($\gamma_{max} = 0{\cdot}01$) of this curve (Smidsrød *et al.*, 1972). The authors choose to use the term $E_{app}$ because there probably exist elements of a dynamic nature in these measurements even at the lowest available compression rate (0·2 mm/s). Based on this slope, apparent Youngs modulus (in N/$m^2$ = Pa) is given by the equation

$$E = [F(g)/A(m^2)]/[\Delta l/l] \times 0{\cdot}0098\ (N/g)]$$

where $F$ is the force (in grams) related to the relative deformation ($\Delta l/l$) of the initial slope of the force/deformation curve, $A$ = surface area of the gel cylinder and 0·0098 is the conversion factor from g to N. The $E_{app}$-values given are based on an average (±STD) of five gel cylinders.

### Dynamic rheological measurements

These measurements were performed by oscillation tests in a Bohlin VOR Rheometer (Lund, Sweden) equipped with a serrated plate–plate measuring geometry. Operational parameters: Frequency 1 Hz, Strain 0·022, Torsion bar 4 g cm, Temperature 20°C. All dynamic tests were performed at 1% (w/v) alginate concentration.

## RESULTS AND DISCUSSION

### Gelling system

Direct addition of D-glucono-$\delta$-lactone (GDL) into a Na–alginate solution reproducibly gave homogeneous alginic acid gels. These gels appear to differ from the Ca–alginate gels in two major ways; they are considerably more turbid and they are 'shorter' in texture (i.e. they break at lower deformation rates compared to Ca–alginate gels, data not included). Apparent maximum in gel strength was reached at 0·8 M GDL for a 1·0% alginic acid gel as seen in Fig. 1. This corresponds to a pH in the final gel ≤2·5. Incubation of these gels in 0·1 M HCl overnight resulted in a levelling off with

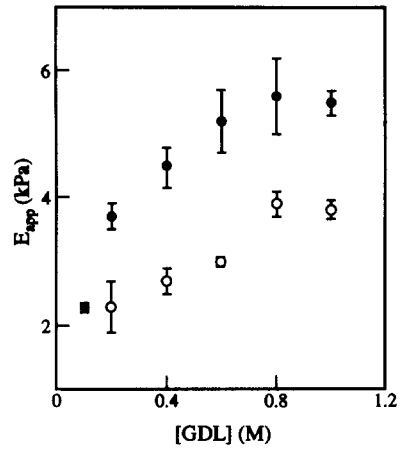


**Fig. 1.** Apparent Youngs moduli estimated for 1% (w/v) alginic acid gels made from sample #2 (●) and sample #9 (○) at different concentrations of D-glucono-δ-lactone (GDL).

respect to $E_{app}$ (not significantly different to $E_{app}$ found at 0·8 M GDL), supporting the fact that 0·8 M GDL is sufficient to obtain maximum acid gel strength at an alginate concentration of 1%.

A series of experiments with different alginate concentrations at a fixed concentration of GDL (0·8 M) was carried out for one of the alginate samples (sample #2). The results are given in Fig. 2(a) and (b). From Fig. 2(a), a critical concentration for gelation can be estimated to about 0·35% based on a linear regression towards $E_{app} = 0$. This value is to be considered as a rather rough estimate because of the probable existence of dynamic elements and the inherent uncertainty of extrapolating to $E_{app} = 0$. However, this value is somewhat higher than the critical concentration for gelation of the same alginate sample as a Ca–gel, where it can be estimated to be just above the critical overlap concentration ($c^* = 2{\cdot}5/[\eta]$) being 0·2% for this alginate sample at ionic strength 0·1 (Martinsen *et al.*, 1989). This deviation is to be expected since the intrinsic viscosity, $[\eta]$, of the alginate sample inevitably will decrease somewhat when pH becomes so low that the uronic acid residues become protonized, although most of the electrostatic contribution to the chain extension is swamped already at ionic strength 0·1 (Haug & Smidsrød, 1962).

From Fig. 2(b), a log–log plot of the same data suggests a concentration dependence of the gel strength close to $c^{1.5}$. This is somewhat lower than for Ca–alginate gels where it previously has been shown to be close to $c^2$ (Smidsrød & Haug, 1972). Whether this deviation is based on measurement uncertainty or a yet unknown property of this particular gel network is at present not clear.

Principally, there exist two major ways to form an alginic acid gel. The first one is already described (by the addition of an acid such as GDL), and the other is by converting a pre-formed Ca–alginate gel (or other gels made with divalent cations) to an acid gel by exchanging the ions with protons. Table 2 shows the apparent Youngs moduli estimated for alginic acid gels made from three different molecular weights of *L. hyperborea* stipe alginates following both routes. Clearly, Ca–alginate gels lose a substantial part of their strength (as determined by the apparent Youngs modulus) when converted to alginic acid gels. At the same time, they also tend to decrease in volume. By adapting the concentration dependence found from the power law modelling of Fig. 2(b) ($E_{app}$ proportional to $c^{1.5}$), values of the apparent Youngs moduli come very close to those found by a direct conversion of a Na–alginate solution to an acid gel by the addition of GDL. Hence, alginic acid gels differ from Ca–alginate gels in that they seem to have a nature closer to equilibrium; the final properties of an alginic acid gel do not seem to depend on how the gel was formed, contrary to Ca–alginate gels (Smidsrød & Haug, 1972).

## Gel strength as function of chemical composition

Apparent Youngs moduli of alginic acid gels made from alginates of different chemical composition are presen-

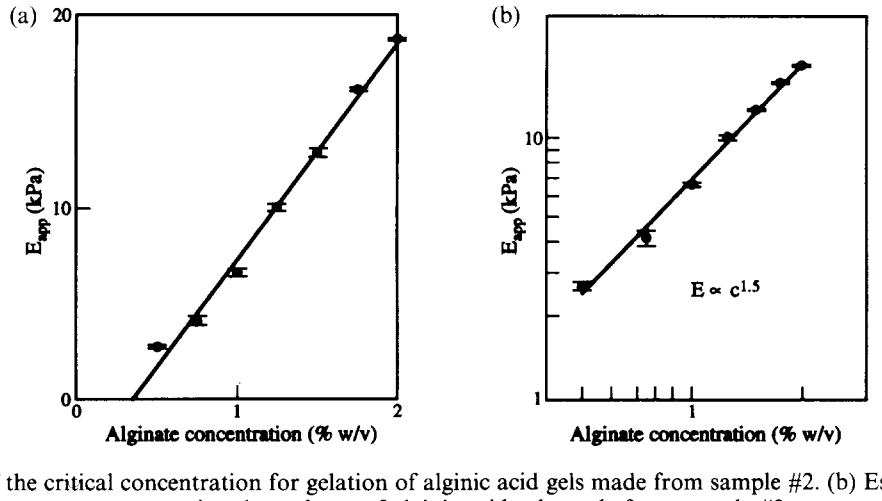


**Fig. 2.** (a) Estimate of the critical concentration for gelation of alginic acid gels made from sample #2. (b) Estimate of the polymer concentration dependence of alginic acid gels made from sample #2.

**Table 2. Apparent Youngs moduli determined for 2% alginic acid gels made of *L. hyperborea* stipe alginates having three different molecular weights. Two different ways to form these gels were tested: (a) a direct addition of GDL, and (b) conversion from a homogeneous Ca–alginate gel (Skjåk-Bræk *et al.*, 1989) to alginic acid gel by an incubation of Ca–alginate gels in several volumes of 0·1M HCl**

| Sample # | Homogeneous Ca–alginate gel | Ca–gel → alginic acid gel | Ca–gel → acid gel Corr: $(V/V_0)^{1.5}$ | Direct addition of GDL |
|---|---|---|---|---|
| 5 | 105 ± 4·6 | 52 ± 4·3 | 15·6 ± 0·3 | 15 ± 1·1 |
| 4 | 116 ± 11 | 64 ± 8·1 | 17·1 ± 1·8 | 17·8 ± 1·4 |
| 2 | 127 ± 6·4 | 79 ± 5·8 | 19·8 ± 1·3 | 20·4 ± 0·7 |

The amount of Ca-ions left in alginic gels made by method (b) was estimated to 0·05% by weight.

ted in Fig. 3. From Fig. 3 it is obvious that chemical composition and sequence to a large extent determine the gel strength. Sample #5 is a *L. hyperborea* stipe alginate with a typical length of guluronic acid blocks larger than 1 ($N_{G>1}$), of about 14, whereas sample #16 is a *P. aeruginosa* alginate with randomly distributed guluronic acid residues implying an average length of mannuronic acid blocks ($N_M$) comparable with the G-block length of sample #5. But although there are comparable lengths of uronic acid blocks, it can be seen that the alginate sample rich in guluronic acid residues gives gels with apparent Youngs moduli six times larger than gels made from the sample rich in mannuronic acid residues. Why mannuronic and guluronic acid blocks are not equivalent in this context is at present not readily explainable and is most probably due to several factors, such as spatial arrangements of the monomers along the polymer chain which is of importance to the formation and stability of intermolecular bonds. It has previously been shown that there are differences in the relative extension between the different building blocks

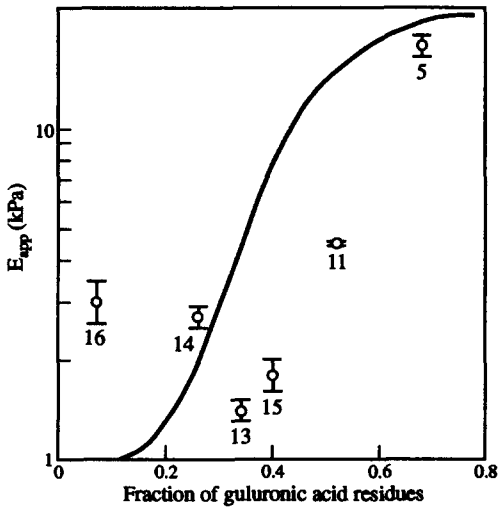


**Fig. 3.** Apparent Youngs moduli of alginic acid gels as a function of guluronic acid content of the different alginate samples. Data point labels refer to sample numbers (see Table 1). Solid line refers to expected results of Ca–alginate gels made from alginate samples with 'normal', non-random distribution of guluronic acid residues (Smidsrød & Haug, 1972).

of alginate molecules (Smidsrød *et al.*, 1973), and against this background, it might be argued that there should be a greater entropy loss when more flexible mannuronic acid blocks are lined up in junctions compared with the more rigid guluronic acid blocks which should make formation less favourable. The difference in $pK_a$ values between the two monomers does not seem to explain this difference in gelling behaviour, since no significant increase in apparent Youngs moduli was observed when sample #9 (*L. hyperborea* leaf alginate) was incubated overnight at pH 1. Further evidence for the fact that G-blocks are more effective than M-blocks in giving gel strength comes from the result that sample #11 (*L. hyperborea* leaf alginate) gives gels which are four times lower in Youngs modulus than alginic acid gels made from sample #4 (*L. hyperborea* stipe alginate). Typical values for $N_{G>1}$ for these types of alginate are 8 and 14, respectively.

From Fig. 3, it is also seen that a high fraction of alternating sequences does not seem to be compatible with high gel strength. At 1% concentration (data not included), sample #13 (*D. antarctica* alginate, $F_{GM/MG} = 0{\cdot}21$) did not give measurable gels at all, whereas sample #14 (from fruiting bodies of *A. nodosum*) gave measurable gels due to the relatively higher fraction of homopolymeric blocks. These two samples are not very different with respect to monomeric composition. At 2% concentration, all samples with a high fraction of alternating sequences gave low strength but measurable gels; even the strictly alternating sample #15 (*P. aeruginosa*, $F_{GM/MG} = 0{\cdot}40$). Most probably, the reason for low gel strength of highly alternating alginates is the lack of homopolymeric sequences which in turn makes it difficult to create stable, intermolecular bonds.

Compared to Ca–alginate gels, it is, as already mentioned, obvious that there must exist other building blocks than polyguluronate to account for the observed results. Samples #15 and 16 would not give a Ca–alginate gel at all due to the complete lack of guluronic acid blocks (Smidsrød & Skjåk-Bræk, 1990). Since homopolymeric regions seem to be essential for alginic acid gel formation, it is reasonable that cooperative processes are involved in the stabilization of intermolecular junctions. It is therefore also reasonable to believe that

there must exist a minimum length of guluronic acid blocks for the formation of one single stable crosslink point, as proposed for Ca–alginate gels ($LG_{min}$, Stokke *et al.*, 1991). But the picture in the case of alginic acid gels becomes somewhat more complicated because consideration must be taken that there probably also exists a $LM_{min}$ (sample #16) and, in the case of strictly alternating sequences, a $L(MG/GM)_{min}$ (sample #15) since both these samples showed a sol–gel transition after the addition of GDL. The fact that sample #16 gave slightly but significantly stronger gels than sample #15, combined with the much higher moduli observed for alginates rich in guluronic acid residues, suggests that the effectiveness of the different building-blocks with respect to alginic acid gel formation seems to be GG > MM ≥ MG/GM. The minimum length of each of the three types of building-blocks capable of forming stable junction-zones is therefore most probably $LG_{min} < LM_{min} \leq L(MG/GM)_{min}$.

Even though the number of consecutive guluronic acid residues necessary to form a stable crosslink ($LG_{min}$) for alginic acid gels is unknown, we can obtain an impression of its relative size compared to Ca–alginate gels by making an assumption that $LG_{min}$ for alginic acid gels has the same significance as proposed for Ca–alginate gels. The results in Table 2 clearly showed that Ca–alginate gels lost a substantial part of their strength when converted to alginic acid gels. Assuming that the number of cross links per volume unit determine the gel strength rather than the strength (energy) of each crosslink (Stokke *et al.*, 1991), the size of $LG_{min}$ giving stable crosslinks in alginic acid gels certainly must be larger than $LG_{min}$ for ionically stabilized crosslinks. However, the formation of microcrystalline gel zones cannot be ruled out due to the observed turbidity of the alginic acid gels. In this case, the reduction in gel strength following the conversion from a Ca–alginate gel to an alginic acid gel can be attributed to a lowering in the number of effective crosslinks per volume unit.

**Gel strength as a function of molecular weight**

Apparent Youngs moduli of alginic acid gels made from *L. hyperborea* stipe and leaf alginates are presented in Fig. 4(a). Gels made from sample #12, i.e. the lowest molecular weight of leaf alginate, were so weak even at 2% concentration that they did not hold their own weight and were hence not measurable in this system.

Figure 4 shows that a molecular weight dependence exists, and that this dependence is more profound for *L. hyperborea* stipe alginate than for alginates isolated from the leaves of the same kelp. The molecular weight dependence thus seems to increase with increasing ability for alginic acid gel formation. A plateau range for molecular weight independency with respect to gel strength is not found within the molecular weight regime studied. It seems, however, that at around 200 kDa, gel strength of gels made from *L. hyperborea* stipe alginates becomes less dependent on molecular weight. Figure 4(b) shows the dynamic storage moduli ($G'$) 24 h after gelation and confirms the general trend from the apparent Youngs moduli in Fig. 4(a). A comparison of the data in Fig. 4(a) and (b) ($E_{app}$ against $E_{app}$ and $G'$ against $G'$) also reveals that the strength of weak gels tends to be over-estimated in the compression measurements due to the inertia of the Stevens Analyzer and also most probably the existence of dynamic elements; on average, the ratio between the moduli of stipe and leaf alginic acid gels is around 5 when measured longitudinally, compared with near 20 in dynamic measurements.

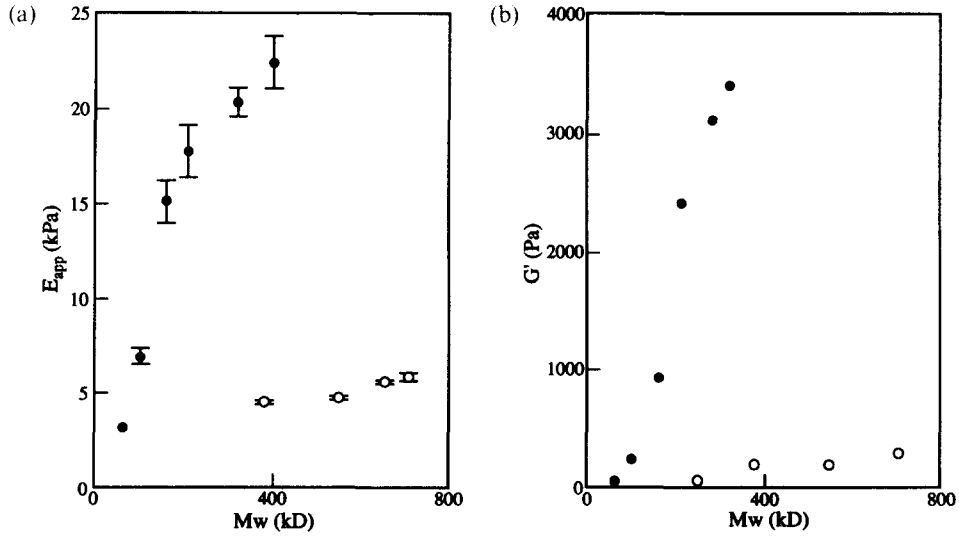


**Fig. 4.** Gel strength of alginic acid gels made from *L. hyperborea* stipe (●) and leaf (○) alginates of different molecular weights as determined by apparent Youngs modulus (a) and dynamic storage modulus (b).

**Gelling kinetics and mechanical characterization**

A strain sweep was performed in order to ensure a linear stress–strain response during the dynamic rheological measurements used in these tests. This scan is presented in Fig. 5, where the dynamic storage modulus ($G'$) as a function of strain is presented for a 24 h old alginic acid gel made from sample #2. Deviation from linearity occurs at strains above 0·06, being well above the chosen 0·022 strain used in the tests. It should be mentioned that the observed deviation from linearity tended to be irreversible, i.e. strains above 0·06 were destructive.

Only two of the samples (#13 and #15) differed from the rest with respect to the time at which the sample changed from a predominant viscoelastic liquid to a viscoelastic solid (i.e. arctan $(G''/G') = \delta = 45°$). These two samples had a transition-time between 60 and 90 min whereas the other samples showed a transition between 20 and 40 min after introduction of D-glucono-$\delta$-lactone (GDL) into the Na–alginate solution (data not shown).

Figure 6 shows the gelling kinetics ($G'$ and phase angle ($\delta$)) for one of the *L. hyperborea* stipe alginates (sample #6) and one sample (#8) of the *L. hyperborea* leaf alginates. These two samples initially show a similar transitional response although highly different in molecular weight. Figure 6 visualizes how relatively fast the high-guluronate alginates (isolated from stipes) reach an apparent equilibrium with respect to $G'$ compared to alginates with a lower content of guluronic acid residues. Figure 7 shows the relative change in $G'$ with time ($(\partial G/G)/\partial t$) 15–20 h after addition of GDL as a function of molecular weight for both stipe and leaf alginates of *L. hyperborea*. All of the stipe samples, with the exception of #7, show a slope in the range around $10^{-7}$, whereas all the leaf samples are still stable at around $2 \times 10^{-6}$. Actually, another 24 h were necessary for the leaf alginate samples to reach the $10^{-7}$ range. This

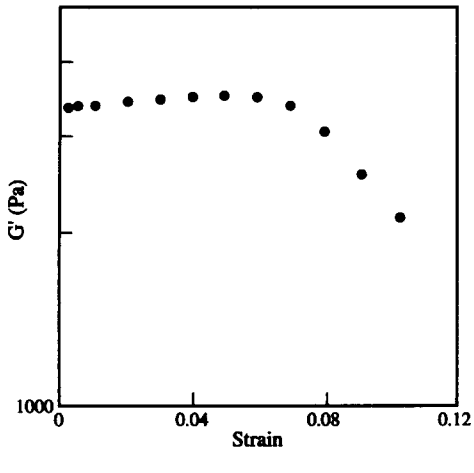


**Fig. 5.** Strain sweep on an alginic acid gel made from sample #2.

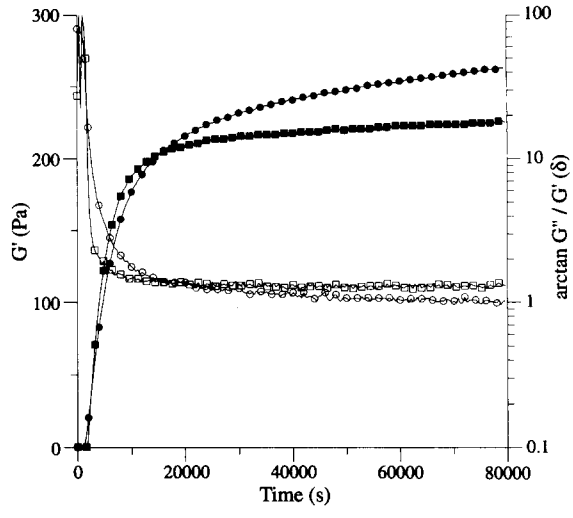


**Fig. 6.** Initial development of $G'$ (closed symbols) and $\delta$ (open symbols) for the alginic acid gel formation of sample #6 (■, □) and sample #8 (●, ○).

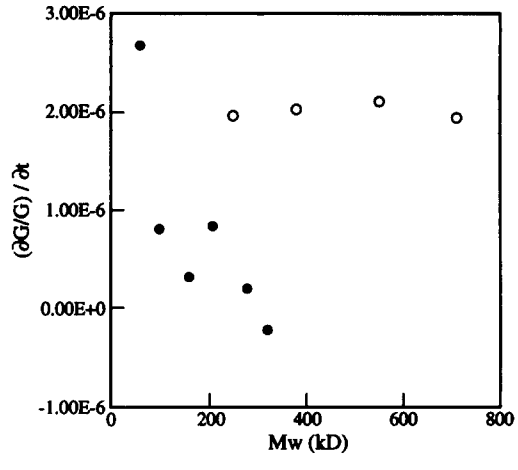


**Fig. 7.** Relative change in $G'$ with time between 15 and 20 h after initiation of alginic acid gel formation for *L. hyperborea* stipe (●) and leaf (○) alginates of different molecular weights.

difference in apparent equilibrium time must be related to the difference in chemical composition, but a detailed discussion of the effect of chemical composition and sequence with respect to gelling kinetics seems premature due to the lack of a detailed understanding of the gelling mechanism.

Figure 8 shows the development within the first 24 h of the dynamic storage modulus ($G'$) and the phase angle ($\delta$) of alginate samples #13 – #15. Due to extremely low gel strength, 1% *D. antarctica* (sample #13) alginic acid gel was not measurable in the longitudinal deformation test for the determination of apparent Youngs modulus. Figure 6 shows, however, that a transition from liquid-like to solid-like character does occur at 1% concentration, but only to a very low extent. The phase angle is as high as 10° after 24 h with $G'$ close to 10 Pa. This implies that by manipulating with alginate variables such as molecular

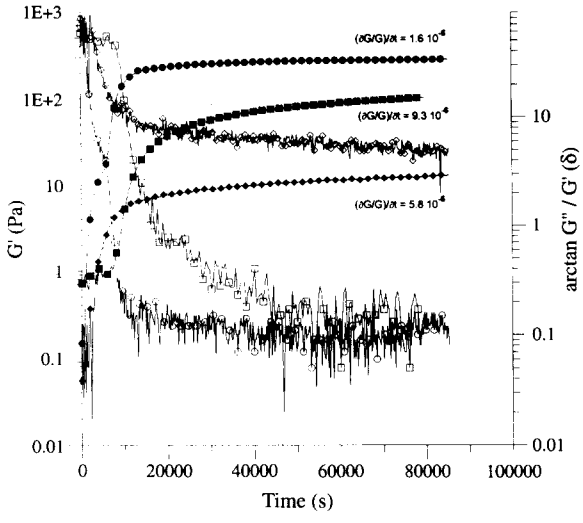


**Fig. 8.** Initial development of $G'$ (closed symbols) and $\delta$ (open symbols) for the alginic acid gel formation of sample #13 (◆, ◇), sample #14 (●, ○) and sample #15 (■, □).

weight and chemical composition, alginic acid gels at the same concentration can be made that differ by a factor well above 300 with respect to $G'$. One should also be aware that sample #15 (strictly alternating *P. aeruginosa* alginate) is close to 10 times higher with respect to $G'$ compared to sample #13. This can be due to differences in molecular weight, but can alternatively be looked upon as an effect of the strictly alternating monomers (40% GM/MG) giving rise to MG blocks that are so uniformly built up that they are able to support the formation of stable, intermolecular crosslinks. Additionally, the slope of $G'$ of the *Pseudomonas* sample after 24 h is much higher than the one of the *Durvillea* sample, implying that the *Pseudomonas* acid gel is under further development to a greater extent giving even larger differences with respect to $G'$ with increasing time. Sample #14 (alginates from fruiting bodies of *A. nodosum*) shows an earlier transitional response and a 20–30 times larger $G'$ compared to the *Durvillea* sample. This difference cannot be related to monomer composition since these two samples are closely related in that sense, but rather to the lack of homopolymeric sequences of the *Durvillea* sample. From Fig. 8, we might therefore draw the conclusion that an increasing fraction of alternating sequences interferes with the formation of consecutive intermolecular bonds due to irregularities within the alginate molecule, but that they, in extreme cases, can take part in stable crosslinks if the fraction of these sequences becomes so high that they themselves can be looked upon as uniform building-blocks (strictly alternating).

Figure 9 shows mechanical spectroscopy results (frequency dependence) of alginic acid gels made from different molecular weights of *L. hyperborea* leaf alginates. With decreasing molecular weight, a power-law modelling shows that the exponent increases; i.e. the gel becomes more frequency dependent, and it is clear from any theoretical consideration that the character of the final gel shifts more towards a viscoelastic liquid with decreasing molecular weight because of the increased fraction of non-elastic chains; i.e. the loose end and sol fractions, having relatively short relaxation times. $G''$ for the sample giving the lowest $G'$ varies with frequency from 0·01 to 4 Pa. This ensures that the term 'gel' can be used for all samples in Fig. 9 within this particular frequency range.

## CONCLUSIONS

Direct addition of D-glucono-$\delta$-lactone has reproducibly been shown to give alginic acid gels that are suited for studies of the importance of polymer variables such as concentration, chemical composition and sequence and molecular weight. Alginic acid gels seem to be less dependent on the history of their formation in contrast to the non-equilibrium nature of calcium alginate gels.

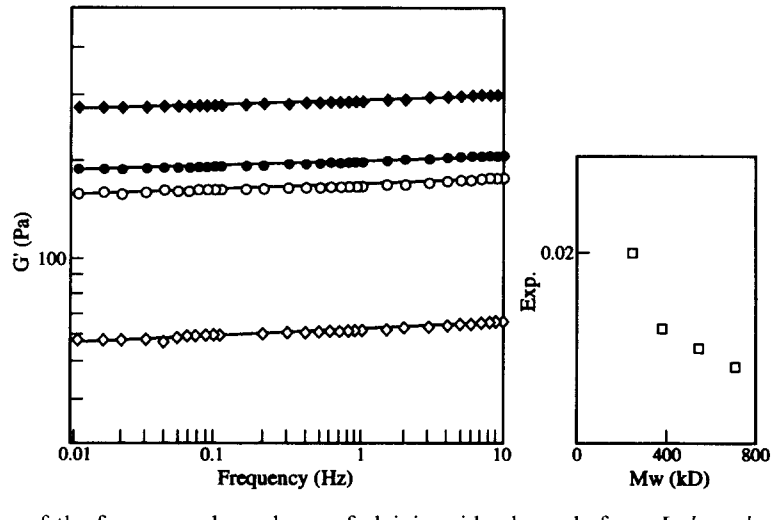


**Fig. 9.** Power-law modelling of the frequency dependence of alginic acid gels made from *L. hyperborea* leaf alginates at different molecular weights.

Chemical composition strongly determines the mechanical properties of the final gel, and as in the case of Ca–alginate gels, guluronic acid blocks are the most effective building blocks for junction formation. Homopolymeric mannuronic acid blocks are also able to support the formation of stable intermolecular crosslinks, although they are much less effective than polyguluronate. Alternating blocks (MG/GM) seem to interfere with the formation of the necessary number of consecutive intermolecular bonds needed to create a stable junction-zone, but in extreme cases, strictly alternating MG/GM-blocks can act as repeating sequences capable of forming crosslinks. There exists a molecular weight dependence which becomes more profound with an increasing ability for alginic acid gel formation.

Gelling kinetics studies reveal that there is a trend towards a faster sol–gel transition followed by an early stage of apparent equilibrium with respect to $G'$ with increasing ability for alginic acid gel formation. As expected, mechanical spectroscopy reveals increasing frequency dependence with decreasing molecular weight.

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